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(54) Contact adhesives

(57) Contact adhesives comprise aqueous emulsions having the following dry component compositions by weight: (1) 100 parts polymer component comprising a terpolymer containing a chlorinated monomer, an acrylic monomer without a reactive functional group and an acrylic monomer having a reactive functional group, the polymer component having a glass transition temperature in the range -18°C to $+10^{\circ}\text{C}$, (2) 10 to 50 parts resin component comprising at least one of: an alkyl phenolic resin, a liquid addition product of an alkyl phenol and formaldehyde, and a terpene phenolic resin, (3) 0.1 to 10 parts emulsifier and (4) 0.01 to 10 parts stabiliser. A crosslinking agent may be included. The contact adhesives are prepared by blending an aqueous emulsion of the polymer component with the resin component in a liquid state, either molten or in solution. The solvent may subsequently be removed by evaporation.

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SPECIFICATION

Contact adhesives

- 5 A contact adhesive is a liquid or paste which can be applied to a surface, for example by brushing or spreading, and will set to form a substantially dry film, and for a certain time thereafter, known as the "open" time, if two such dry films are brought together they will coalesce. Usually, only light pressure is required to bring about this coalescence, which occurs at ambient temperatures, but contact adhesives are known which require heat activation and/or substantial pressure to be applied.
- 10 15 Many contact adhesives are, or include, solutions in organic solvents, and their setting to form the substantially dry film depends upon evaporation of the solvent. One example is that produced by the Applicants and sold under their Registered Trade Mark "Evo-Stik" with the reference number 528, which is a solvent-borne polychloroprene contact adhesive. The growing awareness of the narcotic and other properties of some of the solvents used in these adhesives, and the practice of solvent abuse by inhalation, have given rise to a demand for contact adhesives which have a lower proportion of, or do not include, such solvents. However, contact adhesives which have so far been developed in response to this demand have not matched the performance of those containing organic solvents.
- 20 25 U.S. Patent Specification No. 3,222,419 describes pressure-sensitive adhesives made by blending a non-crosslinking resin with a crosslinkable resin. Amongst the non-crosslinking resins exemplified are copolymers of vinylidene chloride with alkyl esters of acrylic or methacrylic acid with the alkyl group containing 2 to 8 carbon atoms. The crosslinkable resins are polymers of the monomeric components of the non-crosslinking resins with a crosslinkable monomer. In producing the pressure-sensitive adhesives, the two resins are dissolved in organic solvents and the solutions are blended. Alternatively, it is proposed that water be added to one or both solutions with vigorous agitation to produce an oil-in-water emulsion before blending and then the solvent may be removed by vacuum distillation to produce a water-based adhesive.
- 30 35 Pressure-sensitive adhesives, when spread and allowed to dry, form films which are tacky to the touch and will adhere to other surfaces. The primary object described in the above-mentioned U.S. Specification is to prepare pressure-sensitive adhesives which display (inter alia) effective properties of tack and tack retention, with ready adhesion to a wide variety of substrates.
- 40 45 In contrast, the dry films produced with contact adhesives, as mentioned above, should not be tacky to the touch and should not adhere to other surfaces. Such properties are, indeed, undesirable in contact adhesives, the dry films of which are required only to adhere to like films, by coalescing as described.
- 50 55 According to this invention, a contact adhesive comprises an aqueous emulsion of a resin component and a polymer component, having the following dry component composition by weight:

polymer component	100
resin component	10 to 50
emulsifier	0.1 to 10
stabiliser	0.01 to 10

- 70 the polymer component comprising a terpolymer containing a chlorinated monomer, an acrylic monomer without a reactive functional group and an acrylic monomer having a reactive functional group,
- 75 the polymer component having a glass transition temperature in the range -18°C to $+10^{\circ}\text{C}$ and the resin component comprising at least one of: an alkyl phenolic resin, a liquid addition product of an alkyl phenol and formaldehyde, and a terpene phenolic resin.
- 80 A crosslinking agent may be included if desired. The acrylic monomer having a reactive functional group may have hydroxyl or carboxylic acid functionality. Suitable examples are hydroxy alkyl acrylates, hydroxy alkyl methacrylates and acrylic acid.
- 85 The polymer component may be a physical blend of a terpolymer as described above with one or more other polymers. Such other polymers need not contain a chlorinated monomer. Examples are styrene acrylate copolymers, acrylic copolymers, vinyl acetate ethylene copolymers (which could include a third monomer), polychloroprene, polyvinyl acetate and vinyl acetate copolymers. The inclusion of one or more of such other polymers enables contact adhesives with improved properties to be obtained. In particular, improvements may be obtained in contactability, water resistance and adhesion to particular substrates.
- 90 95 The contact adhesive is produced by blending an aqueous emulsion of the polymer component with the resin component in a liquid state, as will be described. We have found that best results are obtained by using polymers produced by emulsion polymerisation. Polymers produced by other means, such as bulk or solution polymerisation, and converted into emulsions by stirring solvent solutions with water and then removing the solvent, produce less satisfactory results and are preferably not used.
- 100 105 The emulsifier and/or the stabiliser may be included in the aqueous emulsion of the polymer component during the emulsion polymerisation process or may be added immediately prior to blending with the resin. They improve the thermal and mechanical stability of the emulsions. Even when an emulsifier and/or a stabiliser has been included during emulsion polymerisation, a further emulsifier and/or stabiliser, not necessarily the same as already present, may be added prior to blending.
- 110 115 Additionally, the contact adhesive may contain one or more of the following:
- | | |
|-------------|---------|
| thickener | 0 to 5 |
| plasticiser | 0 to 40 |
| solvent | 0 to 30 |
- 120 Some of the resins which may form, or be included in, the resin component are available in the form of an aqueous dispersion, or emulsion, and these can readily be blended with emulsions of the polymer components by stirring. Emulsion blends produced in this way do not perform very satisfactorily as contact adhesives. However, when the resin component is a
- 125 130

liquid addition product of an alkyl phenol and formaldehyde, it may be incorporated with the polymer component emulsion by stirring, with satisfactory results. Since such liquid addition products are heat-advancing, contact adhesives in which they

form, or are included in, the resin component produce adhesive bonds which are improved by heat or ageing, particularly when a suitable cross-linking agent is included.

Rosin esters, hydrogenated rosins and hydrocarbon resins, sometimes used to improve tack in solvent-based adhesives, do not produce satisfactory contact adhesives when incorporated in aqueous emulsions of the polymer components specified.

The invention further includes a method of manufacture of a contact adhesive as described, comprising the steps of rendering the resin component liquid by heating if necessary and adding an aqueous emulsion of the polymer component (which includes the emulsifier and the colloid stabiliser) with vigorous agitation. As the first portion of the polymer emulsion is added, a water-in-oil emulsion is formed with the resin component as the continuous phase. Inversion occurs as more polymer emulsion is added until finally the resin and polymer components are dispersed in a continuous aqueous phase.

If the resin component is such that heating to a temperature above 100°C is required to render it liquid, the method must be carried out under pressure sufficient to elevate the boiling point of water above that temperature.

A solvent or plasticiser may be added to the resin component to reduce the melting point in a known manner. Alternatively, the resin component may be rendered into a liquid form by dissolving in a solvent. The amount of solvent required for such purposes is substantially less than is used in solvent-based contact adhesives. In most cases, it is advantageous to keep the resin component in a liquid form, either molten or solution, throughout the inversion process. For this purpose, the polymer emulsion may be pre-heated and/or the whole system may be heated. The solvent, or a substantial proportion of it, may be removed by evaporation once the inversion of the emulsion has been achieved.

In a preferred method, particularly beneficial when the polymer emulsion is stable in a low pH (i.e. less than 7) environment, the emulsion of the polymer component is divided into two portions. Ammonia is added to both portions to adjust the pH of the first portion to a level between 7.5 and 9, preferably 8.5, and of the second portion to a level between 4 and 5, preferably between 4 and 4.5. The first portion is added to the liquid resin component with vigorous agitation. Initially, the aqueous emulsion of the polymer component is dispersed in the resin component as a water-in-oil emulsion, but, on continued agitation, inversion of the emulsion occurs as previously mentioned. The second portion is then added with further vigorous agitation. The proportions of the first and second portions should be such that the pH of the resulting product is in the range 5 to 6.

Alternatively, if the polymer emulsion is stable in a high pH environment (i.e. greater than 7), then all the emulsion can be adjusted to an appropriate pH level

prior to adding to the liquid resin.

If desired, other additives required for various purposes, such as thickeners, biocides, antioxidants and crosslinking agents may be added immediately after the addition of the second portion of the polymer component emulsion.

Polymer components having glass transition temperatures within the specified range of -18°C to +10°C provide contact adhesive with good autohesive characteristics. Polymers with glass transition temperatures below this range, being more rubbery in character, produce undesirable tackiness in the dried films and have inadequate strength characteristics to perform as contact adhesives. Polymers with higher glass transition temperatures, on the other hand, would require higher temperature and/or pressure to promote coalescence of the dried films than would normally be expected for contact adhesives.

The resin component is the essential contributor towards the autohesive characteristics of the adhesives. It also improves the adhesion of the dried films to various substrates.

The inclusion of a crosslinking agent may improve the final strength characteristics of the final bond produced by the coalesced dry films and may give improved heat resistance, peel strength and water resistance. A crosslinking agent may promote crosslinking of the acrylic monomer having a reactive functional group, in the aqueous emulsion or when the adhesive is spread as a film and allowed to dry or in the final bond. Heat may be required in the latter case. As previously mentioned, improvements may similarly be obtained when the resin component is, or includes, a liquid addition product of an alkyl phenol and formaldehyde.

Terpolymer emulsions suitable for producing contact adhesives according to the invention are produced by Imperial Chemical Industries p.l.c. and identified by the Registered Trade Mark "Haloflex" with various suffices and by Scott Bader p.l.c. under the Registered Trade Mark "Polidene". Emulsions sold under the Trade Mark "Haloflex" include terpolymers containing vinylidene chloride, vinyl chloride and one or more alkyl acrylates or alkyl methacrylates and may include an unsaturated carboxylic acid monomer. They are described in the Specifications of British Patent No. 1,558,441, U.S. Patent No. 4,341,679 and European Patent Application No. 0030080. Not all the terpolymers described in those Specifications are suitable for use in performing the present invention, but we have found that by selection amongst these terpolymers a range of contact adhesives can be produced to provide properties comparable with or superior to those of solvent-borne contact adhesives. Particularly useful are the Haloflex "ECL" and "ST" grades, which include terpolymers having molar masses in excess of 1,000,000, compared with figures around 25,000 for other grades.

Suitable crosslinking agents include organic species, for example hexamethoxymethyl melamines such as Cymel 303 or glycol urils such as Cymel 1172. ("Cymel" is a Registered Trade Mark of Cyanamid Corporation.) Alternatively, crosslinking agents including metal salts or complexes may be used. Zinc or zirconium, in both cation and anion complexes, are

preferred. For example, zinc ammonium carbonate, zinc oxide, zirconium oxychloride or zirconium ammonium carbonate. Adhesives including such crosslinking agents can have a usable life in excess of one month. Other crosslinking agents can produce adhesives with shorter usable lives, such as a few hours, and in these cases the crosslinking agent may be added immediately before use. For such adhesives the adhesive and the crosslinking agent may be supplied separately as a two-pack adhesive, for mixing by the user. One example of a crosslinking agent suitable for such a two-pack adhesive is Desmodur KA 8267, which has isocyanate functionality. "Desmodur" is a Registered Trade Mark of Bayer AG.

The invention is illustrated by the following examples. All compositions are given in parts by weight.

EXAMPLE 1

Haloflex ST 296, with pH adjusted to 8 with ammonia	350
Haloflex ST 296, with pH adjusted to 4 with ammonia	378
Resin SP 12 (amyl phenolic resin)	130
Butyl Ethoxyl (solvent)	25
880 Ammonia	1
20% Synperonic Np 30 in water (emulsifier)	20
Collacral VL (thickener)	12
Haloflex ST 296 has glass transition temperature (T _g) (measured by differential scanning calorimetry) of 7°C ± 1°C and solids content 51% ± 1.	95

EXAMPLE 2

Composition as in Example 1 but with the amyl phenolic resin SP 12 replaced by 130 parts of Resin SMD 5205. This is a terpene phenolic resin with softening point 70°C ± 3°C.

EXAMPLE 3

Haloflex ECL 220 with PH adjusted to 8 with ammonia	100
Resin SMD 5224 (circa 70% terpene phenolic resin solution in xylene)	27
20% Ammonium Zirconium Carbonate solution (crosslinking agent)	6
Viscalex AT 55 (inverse emulsion thickener)	1
Haloflex ECL 220 has T _g of -7°C ± 1°C and solids content 55% ± 1.	110

EXAMPLE 4

Haloflex ECL 220, with pH adjusted to 8 with ammonia	100
Haloflex ST 302, with pH adjusted to 8 with ammonia	6
Resin SMD 5224	27
20% Ammonia Zirconium Carbonate solution	6
Viscalex AT 55	2
Haloflex ST 302 has T _g of -7°C ± 1°C and solids content 61% ± 2.	120

EXAMPLE 5

Haloflex ST 304/362 with pH adjusted to 8 with ammonia	103
Resin SMD 5224	27
20% Ammonium Zirconium Carbonate solution	6
Viscalex AT 55	3

Haloflex ST 304/362 has T_g of -9°C ± 1°C and solids content 53% ± 1.

The resins SP 12, SMD 5205 and SMD 5224 are supplied by Schenectady Midland Limited, "Ethoxyl" and "Synperonic" are Registered Trade Marks of Imperial Chemical Industries p.l.c., "Collacral" is a Registered Trade Mark of Badische Anilin & Soda Fabrik., "Viscalex" is a Registered Trade Mark of Allied Colloids.

In all the examples, the adhesive compositions were prepared by adding the Haloflex terpolymer component emulsions to the resin component when the latter was in a liquid state with vigorous agitation, as previously described. In examples 1, 2 and 4, in which two Haloflex emulsions were included, they were added to the resin component in the order indicated in the tables of components.

In order to assess the performance of these examples of contact adhesives according to the invention, the following tests were performed and the results compared with the results of similar tests performed with the solvent-borne polychloroprene adhesive "Evo-Stik 528":

TEST PROCEDURES

1. PEEL TEST: A brush coat of adhesive was applied uniformly to a piece of fabric duck and the volatile carrier was allowed to evaporate at ambient temperature for 1 hour. A second coat of adhesive was then applied and after a further drying period of 1 hour two pieces of coated duck were laminated together using the following techniques:

Cold blend—30 seconds under a pressure of 60 p.s.i. (approximately 4.2 Kg/cm²).

Heat activation—the coated pieces were heated for 10 seconds under a radiant heater so that the adhesive surfaces reached 70—80°C followed by pressing together for 30 seconds at 60 p.s.i.

25mm width specimens were then aged for 7 days at 20—25°C prior to testing in a SATRA peel tester (90° peel test). Results are in Newtons/25mm width of bonded specimen.

2. CREEP TEST: Laminated pieces prepared as for the Peel Test were conditioned for 7 days at 20—25°C. The bonded specimens were then conditioned in an oven at 60 ± 1°C for 30 minutes prior to suspending static weights in a T peel configuration. The length of bond (in mm) which separated in one minute is recorded (width of bond 25mm).

3. SUBJECTIVE TEST: A thin uniform film of adhesive was applied to 150mm × 150mm pieces of chipboard and "Formica" laminated plastic sheet and allowed to dry for one hour. The adhesive surfaces were brought together using light hand pressure. The strength of the bonded assembly was assessed immediately using the subjective scale

0 = no coalescence
10 = very strong bond, substrate failure before adhesive failure

RESULTS

	Evo-Stik 528 (Control)	Examples				
		1	2	3	4	5
Peel Test Cold Bond	120	—	—	100	100	90
Peel Test Heat Activation	130	130	120	—	—	—
Creeps 0.5kg	0.2	0.5	2	0.4	0	0
Creeps 1.5kg	3.4	5	5	3.6	3	1
Creeps 2.5kg	8.6	10	7	8.0	11	6
Subjective	8-9	1	1	8	7-8	8

NB Examples 1 and 2 were used as contact adhesives under heat activation conditions.

NB Examples 3—5 were used under cold blend conditions.

5 CLAIMS

1. A contact adhesive comprising an aqueous emulsion of a resin component and a polymer component, having the following dry component composition by weight:

10	polymer component	100
	resin component	10 to 50
	emulsifier	0.1 to 10
	stabiliser	0.01 to 10

15 the polymer component comprising a terpolymer containing a chlorinated monomer, an acrylic monomer without a reactive functional group and an acrylic monomer having a reactive functional group, the polymer component having a glass transition temperature in the range -18°C to $+10^{\circ}\text{C}$ and the resin component comprising at least one of: an alkyl phenolic resin, a liquid addition product of an alkyl phenol and formaldehyde, and a terpene phenolic resin.

25 2. A contact adhesive as claimed in Claim 1 including a crosslinking agent.

3. A contact adhesive as claimed in Claim 2 wherein the crosslinking agent is of an organic species.

30 4. A contact adhesive as claimed in Claim 2 wherein the crosslinking agent comprises a metal salt or complex.

35 5. A contact adhesive as claimed in Claim 4 wherein the crosslinking agent comprises zinc ammonium carbonate or zirconium ammonium carbonate.

40 6. A contact adhesive as claimed in any preceding claim wherein the acrylic monomer having a reactive functional group has hydroxyl or carboxylic acid functionality.

7. A contact adhesive as claimed in any preceding claim wherein the polymer component comprises a blend of a said terpolymer and at least one other polymer.

45 8. A contact adhesive as claimed in Claim 7 wherein the said other polymer is selected from styrene acrylate copolymers, acrylic copolymers, vinyl acetate ethylene copolymers (which may include a third monomer), polychloroprene, and polyvinyl acetate and vinyl acetate copolymers.

9. A contact adhesive substantially as hereinbefore described with reference to any one of the Examples.

55 10. Method of manufacture of a contact adhesive as claimed in any preceding claim comprising the

steps of rendering the resin component liquid if necessary and adding an aqueous emulsion of the polymer component with vigorous agitation.

60 11. Method as claimed in Claim 10 comprising the steps of dividing an aqueous emulsion of the polymer component into two portions, adding ammonia to the first of the portions to adjust the pH to a level between 7.5 and 9, adding ammonia to the second of the portions to adjust the pH to a level between 4 and 5, adding the first portion to the resin with vigorous agitation and thereafter adding the second portion with continued vigorous agitation, the proportions of the first and second portions being such that the resulting product has a pH level in the range 5 to 6.

70 12. Method as claimed in Claim 10 or Claim 11 wherein the resin is rendered liquid by heating.

13. Method as claimed in Claim 10 or Claim 11 wherein the resin is rendered liquid by dissolving in an organic solvent.

75 14. Method as claimed in Claim 13 including the final step of removing a substantial proportion of the organic solvent by evaporation.

15. Method as claimed in any of Claims 11 to 14 wherein the pH of the first portion is adjusted to 8.5.

80 16. Method as claimed in any of Claims 11 to 14 wherein the pH of the second portion is adjusted to a level between 4 and 4.5.

17. Method of manufacture of a contact adhesive substantially as hereinbefore described.

85 18. A contact adhesive as claimed in any of Claims 1 to 9 made by the method claimed in any of Claims 10 to 17.